On the Complexity of Alcoholic Beverages & Origins of Flavor Components: A Brief Characterization and Sensory Evaluation of Ten Key Volatile Compounds

Gary Spedding, Ph.D.
Brewing and Distilling Analytical Services, LLC
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www.alcbevtesting.com
Overview

Alcoholic Beverage Production
Complex Beverages
Flavor Production (Origins)
Opportunities for flavor addition, and improvement and development of new or enhanced flavored products
Set of 10 Key Flavors presented as aroma bottles
Complex Beverages - Types

Coffee

Tea? [Classic teas – not flavored]

Beer

The “Brown Liquors” (Trad. Distilled Spirits)

Whiskies, Rums, Aged Tequilas

Wine?
“A complex beverage is one that has not (yet) been formulated from a limited set of core components and presented to a trained sensory panel or to consumers with a resounding positive identification and acceptance of authenticity of that product style or class.” [So far such formulations do not have the right “Amplitude”]
Thoughts - I

- “A characteristic and sound flavor in a beer, wine or distilled beverage can only rarely be associated with specific compounds.”

- “Perceived odor sensation - evoked by many different compounds together.” [Quality/flavor complex] Is it a positive marriage? Amplitude/Trueness to Brand

- If not and flavors are out of specification or unpleasant >> Product rejection!
Thoughts - II

- Flavors – desirable/undesirable or in/out of specification – depends on concentration and detection thresholds & Synergistic/Antagonistic effects (enhancement & masking).

- The actual amount of each component is less important than its aroma threshold. Yet volatility is important.

- Tactile sensations & other factors at play.
Why the Complexity?

As with the discussion on coffee:
Many ingredients/steps involved – (incl. biological processes) > leading to extraction, formation and interaction of over 1000 components (1300+?)
Core set (a few dozen?)
> 100’s other sub-threshold [all chemical classes!] components with antagonistic or synergistic relationships raise the base to give the desired sensory response
Brewing - Malt - The Soul of Beer & Spirits

<table>
<thead>
<tr>
<th>Malt</th>
<th>Flavour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green malt</td>
<td>Green, grassy, green pea</td>
</tr>
<tr>
<td>Lager malt</td>
<td>Green, malty, nutty, sweet</td>
</tr>
<tr>
<td>Ale malt</td>
<td>Malty, nutty, sweet, toasted</td>
</tr>
<tr>
<td>Caramelised</td>
<td></td>
</tr>
<tr>
<td>Caramalt</td>
<td>Sweet, caramel</td>
</tr>
<tr>
<td>Crystal</td>
<td>Sweet, caramel, stewed fruit, toffee, black treacle, burnt</td>
</tr>
<tr>
<td>Roasted (dry)</td>
<td></td>
</tr>
<tr>
<td>Amber malt</td>
<td>Biscuity, baked, malty, bitter</td>
</tr>
<tr>
<td>Chocolate malt</td>
<td>Dark chocolate, burnt, sharp</td>
</tr>
<tr>
<td>Black malt</td>
<td>Burnt, black coffee, sharp, some acrid</td>
</tr>
<tr>
<td>Roasted barley</td>
<td>Burnt, sharp, acrid, dry, black coffee</td>
</tr>
</tbody>
</table>

Briess Malt Flavor Wheel

©2001 Briess Malting Company
Chilton, Wisconsin USA
Brewing - Hops

2-METHYLBUTYRIC ACID - CHEESY
3-METHYLBUTYRIC ACID - ISOVALERIC - CHEESY
MERCAPTO COMPOUNDS - BLACKCURRANT & GRAPEFRUIT

ALPHA-PINENE - PINE, HERBAL
BETA-IONONE - FLORAL, BERRY
BETA-PINENE - PINE, SPICY
CARYOPHYLLENE - WOODY
CIS-3-HEXENAL - GREEN, LEAFY
CIS-ROSE OXIDE - FRUITY, HERBAL
CITRAL - SWEET CITRUS, LEMON
CITRONELLOL - CITRUSY, FRUITY
ETHYL ESTERS (BUTYRATE/PROPAANOATE PENTANOATE) - FRUITY, PINEAPPLE
FARNESENE - FLORAL
GERANIOL - FLORAL, SWEET, ROSE
HUMULENE - WOODY, PINEY
LIMONENE - CITRIC, ORANGE
LINALOOL - FLORAL, ORANGE
MYRCENE - GREEN, RESINOUS
NEROL - ROSE, CITRUS
TERPINEOL - WOODY

LUPULIN GLANDS
Yellow sticky globs of essential oils and resins that are the main source of aroma and bittering compounds in beer.

STRIG
The stem extending through the cone, where bracteoles originate.

BRACTEOLES
Protective leaves of the hop cone that yield more oil and resin, in addition to tannins and polyphenols.
On the Origins of Flavors

- Raw Materials
- Water
- Yeast and Fermentation
- Microbial Flavors – desirable use of or contaminant organisms
- Stills, shape-structure, materials
- Maturation/Aging
Raw Materials

- Barley (Sp. Malts)
- Corn
- Rye
- Wheat
- Grapes
- Stone Fruits
Microbiological Issues

- Microbiological issues
  - Desirable organisms – Lactic acid bacteria (acidification)
    - Beer - Sour/Lambic/Brett beers
    - Bourbon – sour mash
    - Rum – butyric flavors
  - Contaminating organisms – unwanted flavors
  - Choice of yeast strain
Fermentation

- **Yeast and Fermentation**
  - Most important source of beer flavors and congeners or congener precursors
  - Conditions important/yeast strain
  - Vicinal diketones issue

- **Microbial “friend or foe?”**
  - Lactic acid bacteria – contamination or desirability (MLF in wine included)
**Yeast Metabolism: Key Beverage Flavors**

- **Carbohydrates**: Glucose → Pyruvate → Acetyl-CoA → Ethanol
- **Amino Acids**: Ala, Val, Leu, Ileu, Phe, Tyr
- **Keto Acids**: Forming Acetaldehyde → Ethanol
- **Fatty Acids**: Forming Esters
- **Higher Alcohols**: Forming Esters

**Key Flavors**:
- **Acetaldehyde**: Ethanol
- **Others**: 1-Propanol, 1-Butanol, 2-Methyl-1-propanol, 2-Butanol, Ethyl acetate, 2-Phenethyl acetate, Ethyl octanoate, Ethyl decanoate, Et. dodecanoate, Ethyl lactate

**Methanol** also plays a role in alcoholic beverages and flavor.
Introducing the flavors
We start the presentation of 10 key flavors in the form of aroma bottles. The assessments are spread out through the presentation.

Please carefully evaluate (a couple sniffs) of each compound and relate to the notes provided in the handout.
The Flavors/Classes

Acetaldehyde [Aldehydes]
Butanedione - Diacetyl [Ketones]
Butyric Acid [Acids/Fatty acids]
DMS [Sulfur – sulfides]
Ethyl Acetate/Ethyl Hexanoate [Esters – aliphatic]
Eugenol [Phenols]
Fusel Oils [Higher Alcohols]
Phenethylacetate [Aliphatic-Aromatic group Ester]
Whiskey Lactone [Lactone]
First Three Flavor Notes

- Acetaldehyde – of Apples and Florists!
- 2,3-Butanedione (Diacetyl) Where is the Butter Popcorn?
- Butyric Acid – Ah, Cheesy Babies!
Flavor Notes 4 to 6

- Dimethyl sulfide – of Corn and Oysters!
- Ethyl acetate – Painting the House? Cleaning your nails?
- Ethyl hexanoate (caproate) Turning Cheese to Fresh Red Apples and Spice – nice!
On to Distillation – Interlude: Stills

- (Pot or Column): shape-structure, materials (copper)

- Operation of (The art and skill of each distiller:
  - Extent of heads and tails removed during first cut/ # of distillations, recycling of cuts

- Different flavors/different concentrations from Continuous distillation?
Still life:

Aerated wash – more reactive with copper surfaces of the stills -- reduces the amount of sulfury off-notes

Soluble copper compounds and complexes form with oxygenated mash that react with and remove sulfur compounds

Location of copper as most sulfur removal occurs at phase change
Heads or Tails?

- Heads (Fore-shots):
  - SO2, Acetaldehyde, Ethyl acetate

- Tails (Feints or After-shots):
  - Cutting out the fats (and the fusels)
  - Ethyl esters of caprylic and caproic acids
    - Caproic (C6), Caprylic C8) and Capric (C10) acids
  - Fatty acids: Soapy, goaty, fatty aromas
  - Ethyl esters: Sweet, fruit, oily
Maturation

“The specific combination of one type of distillate (or wine or beer) with any one type of cask leading to the development of a flavor profile relative to time.”

As brewers get creative, think about the original spirit or wine in the cask.
Maturation - Oak

Seasoned, toasted and charred oak – more complexity:

- Hemicelluloses > Wood sugars/caramelization/toasty notes/color
- Lignin > Vanillin/Vanillic acid
- Oak tannins > Astringency – off notes – rubbery
  Oxidized to quinones and H₂O₂
- Char layer – toast and charring >> burnt wood flavors: vol. phenols, guaiacols, cresols and eugenol (smoky, burnt, medicinal notes)
Flavor Notes 7, 8 and 9

- Eugenol – Cloves and cinnamon – toasted staves!

- Fusels – spicy pungency – keep it down please.

- Phenylethanol – smell the roses - fusels not so after all? A mask in disguise?
Maturation

- Maturation: time, rxns, temperature, pH, acidity
- Fill strength-extraction
- Wood composition and preparation (toast/char)
  
  Casks: #Times used/Previous contents!

- New compounds – flavor congeners in maturing spirit
  
  Storage wooden casks gives rise to whisky lactone, vanillin, guaiacol, eugenol, cresols >> migrate from the wood to the spirit

- Loss of Compounds (e.g., sulfurs lost)
Who is in the Wood?

Acids – hint of vinegar!
Aldehydes – leafy and floral
Sulfury – meaty and rubbery
Oily – nutty butter anyone?
Sweet – honey and vanilla – nice!
Woody – resiny and piney
Lactones – coconut and more
Phenolics – wood smoke, cloves and medicinal
Feint of heart – a tail here? – leather and tobacco and goats?
Don’t lose your heads. Estery – fruity and fragrant

A lot goes into the barrel and a lot of action goes on in the barrel – who goes where – who goes there? Who stays to play with your taste buds and delight your aroma sensors?
Whisky lactone – let’s hear it for the coconuts

Where the wood hits a positive lipid note
But the benchmark must be right – isomers at play
Wrapping up the maturation
Aroma evaluation: Summary

Presented 10 key flavors in the form of aroma bottles. Aroma bottles with a cotton plug soaked in alcohol to give a spirit base-note and “spiked” with pure compounds provide a starting point for sensory evaluation of flavors. For beer a standard beer is soaked into the cotton.

The flavors represent most classes of chemical compound

The origins of many of these flavors were discussed during the aroma evaluation sessions
Conclusions - I

Beer, (Ciders - Kombuchas) Spirits (Liqueurs) and Wine
> The most complex beverages known.

Unlikely they will ever be “recreated” from a base set of chemical spps.

Too many steps, ingredients, processes and biology to reduce it to a formulaic operation.

However, (value-added) opportunities may exist to use pure flavors in such type beverages.

Such flavors will need to be pure, added at the right stage and interact well with base worts, aged spirits and barrel aging/aged beers to work well. To date many experiments have given an artificial note to such type alcoholic beverages.
Conclusions – II – Opportunities?

Beer: Hop oil additions for complexity – especially for reduced isomerized bittering acids? (Stream worts – flavor additions) Fruit beer/malternatives formulations? Coffee and chocolate-flavored beers?

Barrel aged beers – use of wood chips/staves etc., along with flavor components?

Flavor matching for non-alcoholic beers?

Spirits: Rapid aging techniques <> not a true flavor match? Suspected need for blending naturally aged & rapid aged spirit. Possibility for flavor adjustments?

Color adjustments by caramel and other (safer?) colorants?

Honey flavored spirits – plagued by haze issues from use of natural product – contaminated with insect body parts. Cleaner flavor components?

White Spirits: GNS for flavored Vodka and Gin (The No. of ingredients for Gin on the rise – must marry well with juniper or create new types/styles?)

General: Natural antioxidant flavor components to maximize shelf-life? (Herbs? Refer to old pre-hopped “Ales”)
But wait – There is More!

Alcoholic beverages are the most complex liquids known! More is learned every day.

The team at BDAS, LLC is available to answer questions on the topic presented here and other questions of concern regarding alcohol beverage production and analytical measurements.

As for the food industry sensory evaluation is an important topic in quality evaluation of beverages and we are ready to address questions or deliver other presentations in this area.

Contact us: info@alcbevtesting.com
www.alcbevtesting.com  859-278-2533